

# Indirect Determination of Fluoride Traces in Natural Waters by Ion Chromatography and ICP-MS Detection

## Application Note

ICP-MS

Environmental

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### Abstract

ICP-MS has been widely accepted as a powerful analytical technique for trace element determination in a wide variety of sample types. The technique is rapid, measures virtually all elements in a single acquisition and has limits of detection typically at or below the ng/L (ppt) level. Even initially problematic elements, such as K, Ca, Fe, As and Se, are now routinely measured using the power and flexibility of the Ar ICP to preferentially remove troublesome spectral overlaps.

However, there are some analytical challenges which cannot be overcome by plasma optimisation, most notably the analysis of elements which are not ionised in the Ar plasma. This Application Note presents a novel method for the indirect determination of one such element, fluorine, where the preliminary data indicates that the ICP-MS measurement is not

4B	5B	6B	7B	0	
				2 4.003 <b>He</b> helium 24 581 54 403 -268.9	1
6 12.01 <b>C</b> carbon 11 256 13500 24 376 4918	7 14.01 <b>N</b> nitrogen 14 53 -209.9	8 16.00 <b>O</b> oxygen 13 614 -218.4	9 19.00 <b>F</b> fluorine 17 418 -219.6 -188.1	10 20.18 <b>Ne</b> neon 21 589 -248.7 31 07 -246.1	2
14 28.09 <b>Si</b> silicon 8 149 1414 16 34 2642	15 30.97 <b>P</b> phosphorus 10 484 44.1 19 72 279.8	16 32.07 <b>S</b> sulfur 10 357 112.8	17 35.45 <b>Cl</b> chlorine 13 01 -101	18 39.95 <b>Ar</b> argon 15 755 -189.2 185.9	3
32 72.61 <b>Ge</b> germanium 7 88 958.5 15 93 2691	33 74.92 <b>As</b> arsenic 9 81 18 63	34 78.96 <b>Se</b> selenium 9 75 220.2 21 5 684.9	35 79.90 <b>Br</b> bromine 11 84 -7.2 21 6 37.9	36 83.80 <b>Kr</b> krypton 13 996 -156.6 24 36 -153.4	4
50 118.7 <b>Sn</b> tin 7 342 232 0 14 628 2270	51 121.8 <b>Sb</b> antimony 8 639 630.7 16 5 1617	52 127.6 <b>Te</b> tellurium 9 01 449.8 18 6 989.8	53 126.9 <b>I</b> iodine 10 454 113.6 19 09 182.8	54 131.3 <b>Xe</b> xenon 12 127 -111.9 21 2 -108.1	5

Fluorine first Ionisation Potential - 17.418 eV

Argon first Ionisation Potential - 15.755 eV

only possible, but offers significant advantages over traditional analytical methods.



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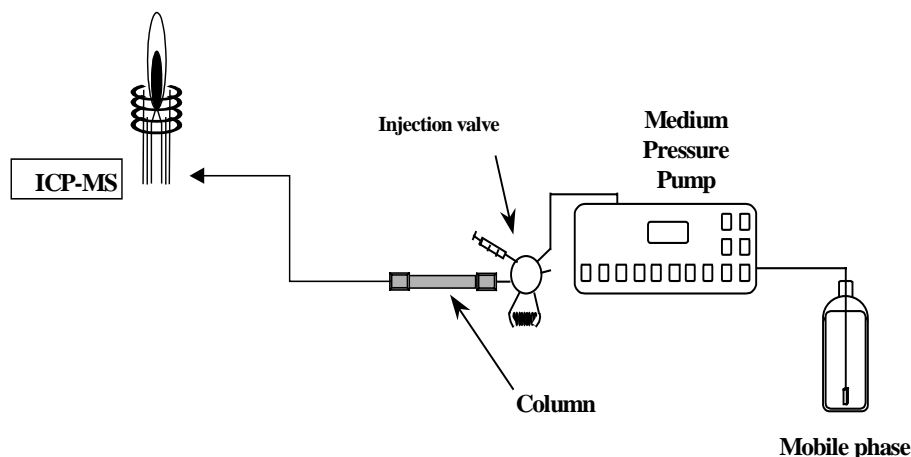


Figure 1 Experimental Set-Up for Fluoride Determination

Table 1 Typical Operating Conditions

Instrument	HP 4500
Rf Power	1300 Watts
Nebuliser	Meinhard
Spray Chamber	Scott type, double pass, room temperature
Sampling depth	5.7 mm
<b>Gas Flow Rates:</b>	
Cool	15 L.min <sup>-1</sup>
Auxiliary	1 L.min <sup>-1</sup>
Carrier	1.17 L.min <sup>-1</sup>
Oxide level (CeO <sup>+</sup> /Ce <sup>+</sup> )	<0.5 %
Doubly charged level (Ce <sup>2+</sup> /Ce <sup>+</sup> )	<1%

## Measurement of Fluoride

During the last decade, the majority of fluoride determinations have been performed using techniques such as potentiometry with fluoride Ion Selective Electrodes (ISE) , ion-chromatography with conductivity detection and, most recently, capillary ISEs has been the preferred technique, but is limited to determinations in the limited to determinations in the mg/L (ppm) range.

The chromatographic separation of Al-fluoride species was first described by Bertsch and Anderson, who

determined the stability constants of several AlF<sub>x</sub> species. In acid aqueous solution, aluminium ions are present as [Al (H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> which can react with F<sup>-</sup> to form the AlF<sub>2</sub><sup>+</sup> complex.

Optimum PH for the complex formation seems to be between 2-4, therefore in the present work pH 2.6-3 was selected, where the complex AlF<sub>2</sub><sup>+</sup> proved to be stable.

Samples and standard solutions were adjusted to pH=3 with nitric acid and spiked with Al<sup>3+</sup> requiring at least a 5-fold weight excess of Al to fluoride to assure that only AlF<sub>2</sub><sup>+</sup> was formed. The samples were

diluted by weight, transferred to 10ml polypropylene test tubes and immersed in a water bath at 50°C for 60 minutes, to ensure quantitative formation of the AlF<sub>2</sub><sup>+</sup> complex. Under these conditions, several parameters were evaluated to obtain selective separation of the complex AlF<sub>2</sub><sup>+</sup> in a 5 cm long ion exchange Dionex Ion Pac Column HPIC-CG2. HNO<sub>3</sub> was found to be an effective eluent for the separation of AlF<sub>2</sub><sup>+</sup> from the excess of Al<sup>3+</sup>. Different molarities of nitric acid, from 0.15 M to 0.75 M, were tested and the conditions chosen for future studies were 0.45 M nitric acid at a flow rate of 0.5 mL/min. The AlF<sub>2</sub><sup>+</sup> complex was measured indirectly by ICP-MS by collecting data for Al at mass 27.

Figure 1 shows the instrumental set-up of the IC-ICP-MS system. The exit tube from the column was connected directly to the concentric nebulizer of the ICP-MS, which can accept flow rates anywhere from 20uL/min to over 2mL/min.

ICP-MS operating conditions are summarised in Table 1.

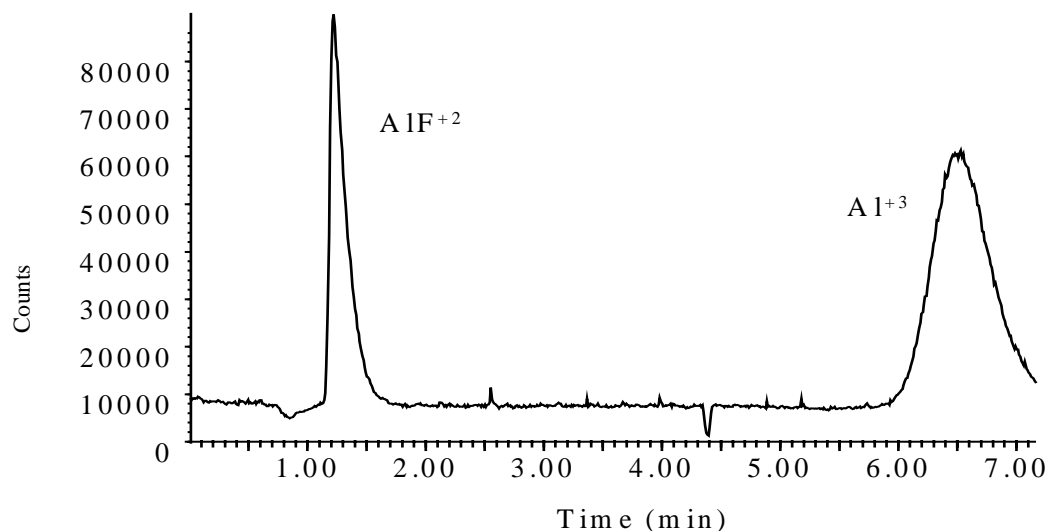


Figure 2 Chromatogram Corresponding to 20 ng.g<sup>-1</sup> F<sup>-</sup>

Table 2 Analytical Characteristics

Analytical Characteristics	ICP-MS Detection
Detection Limit	0.1 ng.g <sup>-1</sup>
Precision	4 % <sup>(1)</sup>
Linear Range	up to 100 <sup>(2)</sup> ng.g <sup>-1</sup>
Regression coefficient (r) (n=7 points)	0.9993

(1) on 5 injections of 20 ng.g<sup>-1</sup> fluoride

(2) using 500 ng.g<sup>-1</sup> aluminium

The chromatogram obtained under these conditions for 20 ng/g F<sup>-</sup> in the presence of 100 ng/g of Al is shown in Figure 2.

As can be observed, two aluminium containing peaks are detected. The first peak could be ascribed to the AlF<sup>2+</sup> complex as its peak height/area was found to be proportional to the

concentration of fluoride in the sample.

### Analytical Performance Characteristis

Analytical performance characteristics are summarised in Table 2. The linear dynamic range for fluoride determination depends on the

aluminium excess added to the sample. It was observed that, for a given aluminium concentration, the upper linear limit for fluoride determinations was about one fifth of the total aluminium concentration. Aluminium concentrations higher than 500 ng/g were not tested, to avoid contamination effects in the ICP-MS. In practice, it should be straightforward to dilute samples to a level of fluoride where Al addition would be at an acceptable level, as shown in this study. Alternatively, ISE could be used as a screening tool, after which the IC-ICP-MS method could be used to determine those fluoride levels which were found to be below the limit of detection for ISE.

The detection limit obtained by the IC-ICP-MS method was 0.1 ng/g, calculated as three times the standard deviation of the blank, divided by the slope of a linear calibration between 0-5 ng/g. As can be observed, the detection limit using ICP-MS detection is one of the lowest ever reported for the determination of fluoride.

Figure 3 shows a typical calibration curve obtained from 5 to 50 ng/g (ppb)

of fluoride and containing 200 ng/g aluminium in each standard solution. The linear calibration demonstrates that the peak area of the complex is proportional to the fluoride concentration. Determination of Fluoride in Fresh and Sea Water Samples.

Under the optimum separation conditions using  $\text{HNO}_3$  for elution, the retention time for  $\text{Al}^{3+}$  is under 7 minutes, allowing a sampling rate of 6-7 samples per hour. To evaluate the use of the proposed ICP-MS method in routine operation, it was applied to the determination of fluoride in natural and drinking waters from a variety of sources and with different saline concentration.

At this time, no stable aqueous fluoride reference material was available, so it was decided to compare the proposed methodology with the fluoride ion selective electrode (FISE). Since many natural water samples contain fluoride levels below the limit of detection of FISE, a spike-recovery exercise was also undertaken.

In order to minimise aluminium addition to the samples and contamination of the ICP-MS, up to 200 fold dilution of some drinking and sea-water samples was necessary. The results obtained are summarised in Table 3.

Some of the water samples contained fluoride levels too low to be measured by FISE (at around 150 ng/g), so comparison between the FISE method and the IC-ICP-MS method was not possible. However, where FISE was able to measure the levels present, good agreement with the IC-ICP-MS results was obtained. In the other cases tested, the spike recovery exercise indicated that the IC-ICP-MS method gave good recoveries (within  $100 \pm 10\%$ ), showing the applicability of the proposed methodology to

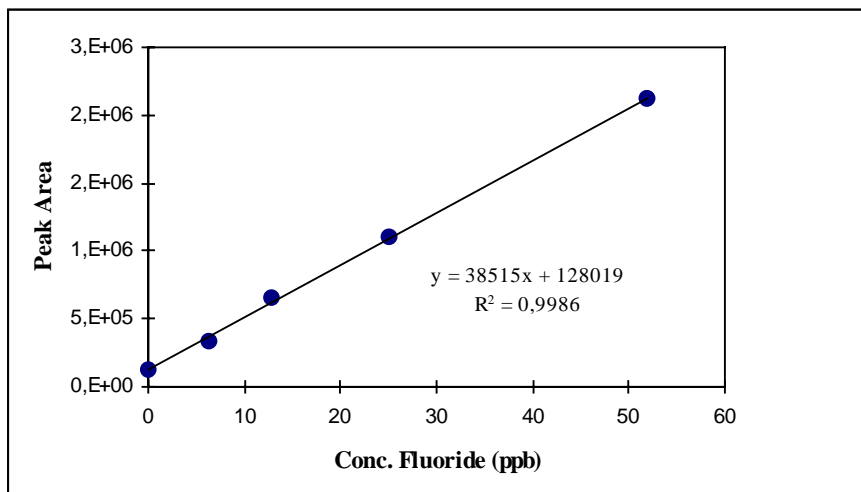


Figure 3 Typical Calibration Curve of Fluoride

Table 3 Results Obtained for Fluoride in Water Samples Using ICP-MS

Water Sample (dilution factor)	Conc. found(n=3) ICP-MS( $\text{ng.g}^{-1}$ )	Conc. found FISE ( $\text{ng.g}^{-1}$ )	Spiked amount ( $\text{ng.g}^{-1}$ )	Recovery (%)
Fontecelta (200)	8050 $\pm$ 80	7700	4300	104
Font-Vella (10)	182 $\pm$ 2	-	205	97.8
Tap-water (10)	161 $\pm$ 1	-	210	90
* Sea-water(100)	1030 $\pm$ 60	1080	1080	97.5

perform fluoride determination at extremely low levels in natural water samples.

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Printed in Japan (02/00)  
5968-8232E